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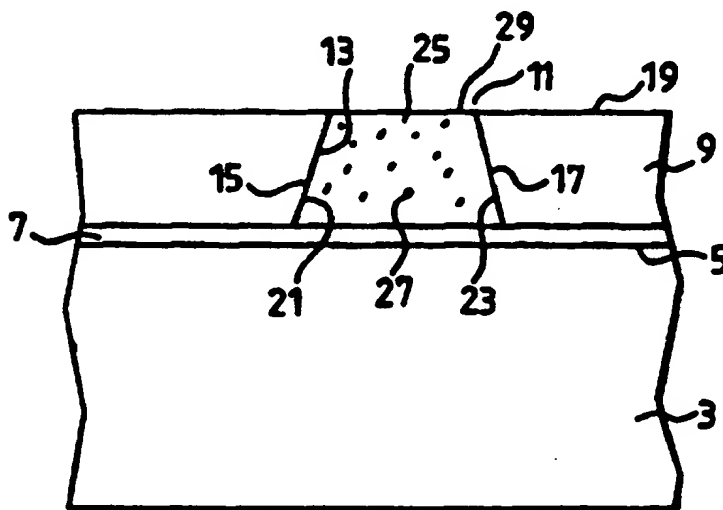
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(54) Title: PRODUCTION OF ELECTRICAL CIRCUIT BOARDS

(57) Abstract

A method of forming a conductive path (11) of an electrical circuit board (1) comprises applying an adhesive (7) to a substrate (3) and applying a conductive ink (25) over the adhesive (7) in a pattern corresponding to the desired conductive path (11). A photoimageable layer (9) can be applied over the adhesive (7) or substrate and subjected to a photoimaging and developing process. This forms a track (13) in the photoimageable layer (9), corresponding to the desired conductive path (11). The conductive ink (25) is introduced into the track (13) prior to heating. The heating affects curing of the adhesive (7) and bonding of the conductive ink (25) to the adhesive layer (7) simultaneously with reflow or sintering of a metallic component (27) of the ink. The ink (25) comprises a metallic component (27) and a flux but is substantially free of any resin or any reactive monomer or polymer.



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PRODUCTION OF ELECTRICAL CIRCUIT BOARDS

The present invention relates to a process for forming a conductive path during the production of electrical circuit boards, such as printed circuit boards, and conductive ink for use in this process.

Conventionally, electrically conductive paths upon printed circuit boards and the like have generally been manufactured by a subtractive method (i.e. by etching away undesired portions of a layer of electrically conductive material - typically copper extending over the surface of a board) or by an additive method (i.e. by building up sequential layers of conductive and dielectric materials upon a substrate).

The subtractive method normally begins with a substrate to which a conductive layer of copper or some other metal has been applied. The conductive paths which interconnect the circuit components are produced by masking the areas of copper or metal required to make up the circuit with a protective layer, usually referred to as resist. When the substrate is sprayed with a corrosive etchant solution the unprotected areas are etched away. Those areas beneath the resist however are protected by it and so remain on the substrate. The resist layer is then stripped away using a suitable solvent or caustic stripping solution to reveal the desired circuit pattern.

The resist layer pattern may for example be defined using a silk printing screen. The resist pattern may also be produced by exposing a photosensitive resist layer to UV radiation through a suitable piece of art-work, such that the pattern required to define the circuit is rendered insoluble in dilute alkaline solutions. The areas not required to define the circuit are soluble in the dilute alkaline solution and so may be washed away, leaving or "developing" the resist in the pattern of the circuit required. The resists used in this application are then generally stripped in caustic solutions.

One specific type of additive process is commonly known as conductive polymer thick film (PTF). This utilises metal filled (PTF) inks to define conductive circuit tracks. It has the benefit of being significantly more environmentally friendly as it does not involve the generation and subsequent processing or disposal of considerable quantities of copper solubilized in etchants. The conductive polymer inks are however very limited in their electrical conductivity and the process is therefore limited to a few specific applications.

Some other additive processes include the use of metal filled inks. The need to ensure that such metallic inks are firmly bonded to the substrates employed means that a fairly high percentage of adhesive resin needs to be included to affect the said bonding. The high bonding resin content limits the electrical conductivity.

One proposal for the combination of additive and subtractive type of process is disclosed in WO 90/12482. In this method, a non-conductive substrate is coated with a film of vacuum sputtered metal. This is then coated with a photosensitive resin which is selectively exposed and developed to produce the desired circuit pattern etched into the surface of the resist. The areas of sputtered metal bared by this process are then plated up with copper by electrodeposition to produce circuit tracks of the desired thickness. The photosensitive resist is then stripped and the sputtered metal layer flash etched away to yield the desired circuit pattern. Subsequently further layers of circuitry may be added by sequentially adding further layers of photosensitive material and sputtered metal and repeating the electrodeposition and etching processes.

Another subtractive process is described in US-A-4 651 417. This uses a substrate which is non-conductive and has been pressed on its surface to produce recesses in the shape of the desired circuitry. The substrate is then vacuum sputtered with a suitable metal and then the circuit built up by electrodeposition. The finished circuit is then produced by physically

removing the copper from the substrate surface by sanding or scraping, to leave the circuitry in the recesses as the conductive tracks on the substrate.

Another process which is additive, is disclosed in WO 88/08337. This process involves selective catalysation of the surface of the substrate to allow circuit patterns to be produced using electrolytic copper deposition. The initial circuit shape being defined by a photoimageable resist.

A more recent proposal for an additive process is described in WO 93/06943. This is based on the use of a conductive ink including an adhesive resin, as alluded to above. Specifically, the ink is a mixture of a relatively high melting point metal powder, solder powder, a cross linking flux and a reactive monomer or polymer. The reactive monomer or polymer system acts as an adhesive for bonding the ink to the substrate after curing/drying. The flux may be selected so as only to be activated at a predetermined elevated temperature.

To optimise the conductivity consideration has been given to forming a conductive ink comprising a mixture of metals which can be sintered together to form a highly conductive circuit or layer. Such systems do have improved conductivity but generally suffer from problems related to the sintering process. This depends very much on the type of 'flux' or wetting agent used to aid the sintering (or reflow) of the said metal particles. The flux needs to remove the oxides formed enabling the sintering process to take place, especially if the composition includes metals which are readily oxidised such as copper. Furthermore copper oxide is a poor electrical conductor.

Typical fluxes are organic and inorganic acids and salts thereof such as stearic acid, hydrochloric acid, amine hydrochlorides and amine resins.

Weak fluxing agents, for example stearic acid (and other organic acids) do not clean the large surface areas of the finely divided metal powders adequately. Therefore strong fluxing agents are required, amine hydrochlorides are an example, but these strong fluxes often have harmful affects on the final composition such as reduction of adhesion and long term stability.

Nevertheless a strong flux is desirable and so the process which is used, as well as the formulation, need to be considered so that the disadvantages of strong fluxes can be negated.

The method of WO 93/06943 seeks to overcome this disadvantage by using a flux which is only activated at the solder melt temperature. Unfortunately, the method described in the latter document still presents a number of disadvantages. First, the high level of organic material incorporated in the conductive ink lowers the conductivity of the final circuit. Moreover, the special temperature sensitive flux yields water during the heating process, leading to bubbling, and hence voids as curing and reflow/sintering progress. The voids lead to even lower conductivity or possibly, total fracture of the inter-component wiring lines formed as a result of the process.

A new process and conductive ink formulation which overcomes the aforementioned disadvantages of the method described in WO 93/06943 has now been devised. This method, according to the present invention, makes it possible to form an additive conductive path of an electrical circuit board, whereby good adhesion of applied metallic formulations can be achieved without the damaging effects resulting from the inclusion of reactive monomer or polymer in the conductive ink. The method generally involves applying an adhesive to a circuit board substrate and applying a conductive ink over the adhesive in a pattern corresponding to the conductive path. Alternatively, or additionally, the conductive ink may be held in place by the creation of a track in a surrounding dielectric material.

Thus, a first aspect of the present invention now provides a method of forming a conductive path of an electrical circuit board, the method comprising applying an adhesive to a circuit board substrate and applying a conductive ink over the adhesive in a pattern corresponding to the conductive path.

Furthermore, a second aspect of the present invention provides a method of forming a conductive path of an electrical circuit board, the method comprising applying a photoimageable layer to a circuit board substrate, subjecting the photoimageable layer to a photoimaging and developing process to form a track in the photoimageable layer, the track corresponding to the said conductive path, and introducing a conductive ink into the track to form a conductive ink pattern.

Preferably, the track is formed with an undercut region in side walls thereof. This is especially advantageous in holding the conductive ink in place, by means of a mechanical dovetail arrangement.

The system provided by the first aspect of the present invention, as well as other aspects of the present invention which will be defined herein below, enables processing of circuits on any base substrate with adequate thermal stability, for example, coated aluminium, aluminium oxide, ceramic or glass substrates. The use of any of the latter offers advantages to the process of circuit manufacture in terms of temperature stability and recycling potential of the completed circuit at the end of its normal life. The use of coated aluminium/aluminium oxide offers significant advantages, especially in chip on board (COB) and similar applications where planarity of the final surface and/or thermal management problems need to be addressed.

The present invention in all its aspects is suitable for forming a single conductive path (wiring line) on a substrate or a more complicated wiring pattern comprising a network of wiring lines included at two or more layers known as a "multilayer circuit".

The method of the first aspect of the present invention preferably comprises a subsequent step of heating the conductive ink pattern to effect a bond to the adhesive and simultaneously to improve the bond between the adhesive and the base material: followed by the reflow or sintering of metallic component(s) thereof. A preferred way of effecting this heating step is described in more detail herein below.

The conductive ink can be applied in the desired pattern by means of a stencil-type arrangement, which is removed before the heating step. For example, a silk-screen printing process could be used.

However when narrow tracks are required, for example of widths below 200 microns it is generally preferred to define the pattern by the further step, after application of the adhesive, of applying a photoimageable layer over the adhesive, subjecting the photoimageable layer to a photoimaging and a developing process to form a track in the photoimageable layer, the track corresponding to the required conductive path (i.e. intercomponent wiring), and introducing the conductive ink into the track prior to the heating step.

The track formed in the developed photoimageable layer can be formed with side walls which become further apart, the greater the depth from the upper surface of the photoimageable layer. In other words, the track is formed with an "undercut". This provides a dovetail anchor for the solid conductive material formed after sintering of the ink.

In cases where the photoimageable material can be formed with intrinsic adhesive properties and with a sufficient quality of undercut, it is possible to dispense with the adhesive layer used in the first aspect of the present invention. Thus, a second aspect of the present invention provides a method of forming a conductive path of an electrical circuit board, the method comprising applying a photoimageable layer to a circuit board substrate, subjecting the photoimageable layer to a photoimaging and developing process to form a track in the

photoimageable layer, the track corresponding to the said conductive path and being formed with an undercut region in side walls thereof, and introducing a conductive ink into the track.

Again, the process according to the second aspect of the present invention is preferably followed by a step of heating the conductive ink in the track, to effect bonding of the ink to the adhesive and reflow or sintering of a metallic component thereof.

A preferred embodiment of the first and/or second aspect of the present invention provides the following steps:-

1. Applying a thin layer of an adhesive to the surface of a non-conductive substrate, by printing a solution of the adhesive onto the substrate and subsequently drying it to give a tack free finish;
2. Applying a coating of photoimageable, developable resist material, drying it to give a tack free finish and imaging the material by selectively exposing areas of the resist to a suitable source of radiation;
3. Developing said image using a mild alkali solution, or other suitable developer to remove the areas of unexposed photoimageable resist;
4. Applying a conductive ink to the surface of the substrate such that the recesses produced in the resist layers by the development process are filled by the ink;
5. Subjecting the substrate to suitable heat treatment to cause the conductive ink to melt and coalesce to form a coherent conductive pattern on the substrate, contained, protected and anchored by the photocurable resist layer. Subsequently, the tracks formed may be soldered or plated to give them protection against oxidative attack. The heating process not only reflows the conductive ink, but also causes the thermal cure of the resist layer and the adhesive bonding layer which is simultaneously cured, attaching the conductive track to the base substrate while remaining insulated from it; and

6. Stripping the surface of extraneous conductive ink either by chemical means, or mechanical abrasion.

Generally preferred are those resists (i.e. materials for forming the photoimageable layer) which are developable by application of a solution of an alkali or of an organic solvent.

Such materials are typically those used for the preparation of photoimageable solder masks and many materials which are commercially available as soldermasks may be used as the dielectric resist in this invention. Typical of these soldermasks are the liquid products sold as Imagecure™ by Coates, Probimer™ by Ciba and PSR 4000™ by Taiyo or dry film products sold, for example, by Dupont, Morton Thiokol, Hitachi and others. Typically the liquid products are supplied as two pack systems although single pack systems such as those described in patent GB-1-2 032 939 may also be used.

A typical formulation for this type of material comprises from 50 to 60% epoxy novolak acrylate resin solution, from 3 to 5% photoreactive monomers, from 4 to 6% photoinitiators, from 25 to 30% inorganic fillers, optionally from 2 to 5% pigment and optionally from 0.5 to 2% defoamers and flow aids. Wherever used herein, unless indicated to the contrary, all percentages are percentages by weight. Optionally a second cross linking component may be added. A typical cross linking agent is made up of an unreacted epoxy resin and cure catalyst dissolved in a solvent and optionally filled with one or a number of inorganic filler materials.

Alkali soluble versions of such resists are typically based on a carboxylated epoxy novolak acrylate resin, produced by reacting an epoxy novolak resin with a mixture of saturated and unsaturated monocarboxylic acids. The hydroxyl groups formed by this reaction are then used to react dicarboxylic acid anhydrides onto the polymer, ring opening them to give free carboxylic acid groups. These confer solubility in mild alkali solutions on the material. This resin is dissolved in an organic solvent in a mixture with radiation sensitive oligomeric materials, photoinitiators, fillers, flow aids, pigments and defoamers.

The carboxylated epoxy novolak acrylate resin referred to in the preceding paragraph may be the reaction product of an epoxy phenol or cresol novolak with a mixture of acrylic, methacrylic, hexanoic or benzoic acids, which may have been carboxylated with maleic, succinic, tetrahydro- or hexahydrophthalic anhydrides. Properties may be further enhanced by the incorporation of further organic acids. The resin being dissolved in a suitable solvent such as propylene glycol diacetate, propylene glycol methyl ether acetate, ethyl ethoxy propionate or dipropylene glycol methyl ether acetate.

The thermal hardening component of the resist typically comprises from 35 to 50% epoxy resin, from 15 to 30% inorganic filler and from 1 to 7% thermal curing catalyst, the balance being solvent. The epoxy resin may be an epoxy novolak resin or a bis-phenol A type epoxy resin like Epikote 1004 (Shell Chemicals). Inorganic fillers which may be used are barium sulphate, talc and silica. The thermal cure catalyst may be an amine compound such as diamino diphenylmethane or dicyandiamide and the solvent may be a glycol ether or ester such as propylene glycol monomethyl ether acetate.

Formulations for suitable photoimageable systems may be as described in GB-A-2 175 908.

The photoimageable resist layer may be applied by a variety of means including screen printing, roller coating, dry film lamination, curtain coating or spray.

The photoimageable resist material will usually comprise a photoinitiator, especially one of a type which preferentially hardens the surface of the photoimageable layer. The use of such materials helps to emphasise the definition of the undercut in the track formed in the developed photoimageable material. Another way of forming a relatively hardened "skin" over the upper surface and undercut walls of the developed photoresist layer is to incorporate therein, a pigment or other solid material for limiting penetration of UV radiation into the body of the layer.

However, it is otherwise desirable that no pigmentation be used in the resist formulation. It can easily be shown that pigments impede the extent of through cure of the photoreactive layer, which may be applied in thicknesses exceeding 75 microns. If such thicknesses are surface cured, solvent(s), from the coating process may remain trapped beneath the surface due to the rapid surface cure of a pigmented system. These solvents can later cause catastrophic blistering and wrinkling of the resist layer during conductive ink reflow. However, the through cure must be such as to leave deliberately undercut side walls thereby entrapping the inserted conductive ink.

If the photoimageable resist layer is applied in two or more separate applications, a laminated structure may be imparted thereto. In this way, at the end of the each step of the process, any excess metal of the wiring lines, above the plane of the upper surface of the circuit board may be removed by appropriate chemical or physical treatment, at the same time removing an upper layer of the laminated photoimageable resist layer to leave a smooth surface.

In any event, the adhesive, photocurable resist material and photoimageable material may all be applied by any suitable process such as screen printing, curtain coating, electrostatic or airless spraying or roller coating.

Regarding the adhesive material used to attach the conductive ink to the substrate in the method according to the first or optionally the second, aspect of the present invention, this may be of a wide range of chemical types. Especially preferred are those which show good thermal stability and a degree of reactivity to epoxy, phenolic or carboxylic acid group containing materials. Materials which typically may be used in this application are; epoxy resins, epoxy acrylates or carboxylates, high melting point polyamide resins mixed with epoxy resins, together with a suitable cure catalyst. These epoxy resins may be materials such as epoxy novolaks or bisphenol-A epoxy resins. These materials are dissolved in organic solvents to render them coatable.

In any event, the adhesive may be a single component adhesive or a two-component adhesive system. Third components are as recited in the preceding paragraph but in any-event, generally speaking epoxy resin, novolak resins, epoxy novolak resins, acrylate resins and polyamide resins are generally preferred, together with a catalyst for effecting curing of said resin at an elevated temperature.

Most preferred are carboxylated epoxy acrylate resins, such as those used for the preparation of soldermasks. High melting point polyamides are also much preferred, such as Versamid 115 (Cray Valley) dissolved in butanol or toluene, also epoxy novolak resins, such as Quatrex 2410 produced by Dow Chemicals. Alternatively bisphenol-A type epoxy resins such as Epikote 1001 (Shell Chemicals), dissolved in propylene glycol diacetate or other suitable solvent. Typically the adhesive composition is made up of a 60 to 70% solids solution of the adhesive resin in solvent. Suitable thermal cure catalysts for the polyamide-epoxy mixture are dicyandiamide and Epikure 143FF (Shell Chemicals).

The thickness of adhesive coating needs to be limited so that it forms a suitable dielectric layer if a conductive base or substrate (such as aluminium) is used but not so thick that it penetrates to an excessive extent into the conductive ink formed thereon and reduces the electrical conductivity of that ink. Preferred adhesive coating thicknesses are in the range of from 4 to 15 most preferably from 8 to 12 microns.

Generally speaking the conductive ink is made up of metal powders rendered to a printable consistency by the addition of liquid fluxes, which will later allow the molten ink to melt and coalesce to give a coherent metallic track

The conductive ink material typically contains 75% total metal powder (e.g. made up of 25% copper powder with 25% each of silver or tin-lead powder), 17% flux material and 8% of a volatile solvent.

The metal powders used typically have a particle size range of 5-15 microns. The flux materials used may be of a proprietary type, such as Alpha flux 850™ (Alpha Metals) or a simple chemical such as glycerol phthalate. The volatile solvent is added to make the ink more mobile and to promote wetting and may be for example acetone, ethanol, methyl ethyl ketone, propylene methyl ether acetate or a high boiling aromatic solvent for example.

The ratio of sizes of the metal powders as well as their composition is of particular significance; this relates to the surface area to be wetted out by the flux and consequently influences both the reflow properties and the final conductivity of the reflowed metal paste.

The relatively low melting point component of the conductive ink preferably has a melting point in the range of from 100°C to 250°C and the relatively high melting point component has a melting point in the range of from 300°C to 1455°C.

Preferably, the relatively low melting point component comprises at least one metal selected from tin, lead, silver, bismuth, antimony and indium or an alloy of at least any two or more of such metals. On the other hand, the relatively high melting point component comprises at least one metal selected from tin, silver, copper, zinc, iron, manganese, nickel and cobalt or an alloy of at least any two or more of such metals.

After elevating the ink to the second temperature, greater than the melting point of the relatively lower melting point component, the resulting wiring line has a higher melting point than that of the aforementioned relatively lower melting point component. Such a line is capable of being conventionally soldered, either with or without prior electroless or other metallic plating.

The heating step is preferably effected by progressively raising the temperature of the conductive ink such that the ink dries at a first temperature and then the metallic component sinters or melts at a second temperature, higher than the first temperature. The advantages of

this progressive heating process can be realised if the ink has a metallic component supported in a flux component and comprises a mixture of metals or alloys, having a relatively low melting point component and a relatively high melting point component.

Typically the adhesive is applied to a thickness of 8 - 12 microns by screen printing, using a fine mesh typically 150T/cm. The coating may also be applied by other means such as roller coating, dip coating or spray. It is unlikely that under most conditions, curtain coating could render a sufficiently thin film reliably, although this is not excluded from the ambit of the present invention.

Preferably, any flux component of the conductive ink comprises a wetting agent and a reactive agent capable of reacting with copper. In that case, it is better for the flux to be made incorporating the wetting agent but excluding the reactive agent, which is then added immediately prior to application.

It will be appreciated that the conductive ink for use in the method according to the first or the second aspect of the present invention differs from that utilised in the method described in WO 93/06943. In particular, it excludes the high level of resin bonding agent of the latter and therefore has a conductivity superior to that of the materials described in the latter document. However, this does not preclude use of resin-containing inks such as described in WO93/06943.

Thus, a third aspect of the present invention provides an electrically conductive composition comprising a metallic component and a flux, the composition being substantially free of any resin or reactive monomer or polymer.

Preferably, the composition according to the third aspect of the present invention is completely free of any resin or reactive monomer or polymer.

The metallic component is preferably a metal powder having a composition as hereinbefore described in respect of the first and second aspects of the present invention and the flux is preferably also as hereinbefore described in that context.

In the context of the third aspect of the present invention, the term "substantially free of an reactive monomer or polymer" preferably means that the amount of (i) resin; or (ii) reactive monomer or polymer; or (i) + (ii) may be independently selected from within a range up to a maximum of any of 25%, 20%, 15%, 10%, 7.5%, 5%, 2.5%, 2%, 1%, 0.75%, 0.5%, 0.25%, 0.2%, 0.1%, 0.05%, and 0.01% by weight of the total composition.

The present invention will now be explained in more detail by way of the following non-limiting examples and by way of the following non-limiting description of a preferred embodiment and with reference to the accompanying drawing in which:-

Figure 1 shows a cross-section through a conductive track on a circuit board substrate, the conductive track being formed by a method according to the present invention.

As shown in Figure 1, a circuit board 1 comprises a board substrate 3, e.g. formed of aluminium or aluminium oxide. Upon an upper surface 5 of this substrate 3 is formed a base adhesive/dielectric layer 7.

A layer of photoimageable resist 9 is then formed on the adhesive layer 7 and photoimaged to define a pattern for the paths 11 of the circuit board wiring.

The developing/processing of the imaged resist layer 9 leaves etched-away tracks 13 therein. The side walls 15, 17 of each such track 13 become further apart, the deeper the distance

15

from the upper surface 19 of the resist layer 9, towards the adhesive layer 7. In other words, undercuts 21, 23 are defined by these side walls 15, 17.

Conductive ink 25 is then introduced into each such track 11 and subjected to a progressively increasing temperature to cure the ink to the adhesive layer and/or sinter the metal particles 27 therein.

It can be seen from Figure 1 that the undercut 21, 23 "key-in", or dovetails the solid wiring line produced by post-heating of the conductive ink.

Further, as mentioned above, it is preferred to form the resist layer 9 as a plurality of discrete layers so that as a final step after cooling, the upper layer (having the surface layer 19 thereon) can be removed together with any excess metal proud of the upper surface 29 of the solid wiring line.

Examples of formulations used to carry out this process and example processing conditions will now be given. In these examples, all percentages are expressed as percentages by weight of the particular mixture or composition in question, unless specifically indicated to the contrary.

EXAMPLE 1

An epoxy resinous material, XV501TSM (Imagecure - Registered Trade Mark), was printed through a 90T mesh, onto a piece of glass epoxy circuit base, and dried for 20 minutes at 90°C to give a thickness of about 8 microns.

A mixture composed of:

16

Copper Powder	75%
2-isoPropyl Ether Acetate	15%
Alpha™ 850 Flux (1)	10%

(1) Organic Acid flux, ex Alpha Metals Inc.

was printed through a stainless steel mesh to give a test pattern, and dried for 30 minutes at 90°C. The resultant circuit pattern had an electrical resistivity of 500×10^{-5} ohmscms. This was then exposed to a temperature of 215°C for 3 minutes and dipped into molten solder at 265°C for 2-3 seconds to give a continuous circuit track with very low electrical resistivity ($<10^{-5}$ ohms cm).

EXAMPLE 2

XV501TSM (Imagecure - Registered Trade Mark) was silk screen printed through a 90T mesh, onto a piece of glass epoxy circuit base, and dried for 20 minutes at 90°C to give a thickness of about 8 microns.

A mixture composed of:

Copper Powder	75%
2-isoPropyl Ether Acetate	15%
Alpha™ 850 Flux	10%

was printed through a stainless steel mesh to give a test pattern, and dried for 30 minutes at 90°C. The resultant circuit pattern had an electrical resistivity of 500×10^{-5} ohmscms. This was then immersed for 10 minutes in commercial immersion tin electroless plating solution and then exposed to a temperature of 215°C for 3 minutes, and dipped into molten solder at 265°C for 2-3 seconds to give a continuous circuit track with very low electrical resistivity ($<10^{-5}$ ohmscm).

The resistivity of this circuit was similar to Example 1 but the tin treatment gave improved solderability.

EXAMPLE 3

Copper Powder	83.45%
65/35 Tin Lead Powder	4.10%
Solid Rosin	2.05%
2-isoPropyl Ether Acetate	10.40%

Processed as Example 1 but gave resistivity values of 10^{-4} ohms cm.

EXAMPLE 4

Copper Powder	50%
Sn-Pb Powder	30%
Organic Flux Glycerol Phthalate	10%
Alpha Flux 850	5%
2-isoPropyl Ether Acetate	5%

Use of alternative Flux to improve printability and solderability.

Processed as Example 1 but gave resistivity values of 10^{-4} ohms cms.

EXAMPLE 5

Copper Powder	71.4%
Organic Flux Glycerol Phthalate	14.3%
Acetone	7.15%
Alpha™ Flux 850	7.15%

18

Use of fast drying solvent to reduce drying time and hence oxidation of copper.

Processed as Example 1 but gave similar results to Example 4.

EXAMPLE 6

Copper Powder	42.83%
Tin Lead Powder (2)	28.57
Organic Flux Glycerol Phthalate	14.30%
Acetone	7.15%
Alpha™ Flux 850	7.15%

(2) 63% Sn, 37% Pb, ex Fry's Metals

Use of tin lead to enhance reflow and solder take-up. Processed as Example 1.

The resistivity of this circuit was similar to Example 1 but the presence of tin lead gave improved solderability.

EXAMPLE 7

Copper Powder	29.5%
Tin Lead Powder	60.5%
Organic Flux Glycerol Phthalate	2.5%
Methoxy Propanol Acetate	5.0%
Alpha™ Flux 850	2.5%

Higher proportion of tin lead powder.

Processed as Example 1 but gave uneven track surface with poor continuity, prior to dipping in molten metal.

EXAMPLE 9

In this case the substrate used was anodised aluminium sheet. A coating of Imagecure™ XV501 TSM was applied to the surface of the sheet to a dry thickness of approximately 75 microns. This photo sensitive surface was imaged to produce slots of various widths. These slots were coated with a thermoplastic resin to about 8 microns dry thickness. A paste made to the formula:

Copper Powder	25%
Tin Lead Powder	35%
Silver	20%
Organic Flux Glycerol Phthalate	5%
Methoxy Propanol Acetate	10%
Alpha™ Flux	5%

When then introduced into the slots and processed as Example 1., the resultant photo imaged track pattern had a resistivity $>10^{-5}$ ohm cms.

EXAMPLE 10

An adhesive formulation made up of 2 parts Epikote 828 (Shell Chemicals), 3 parts Versamid 115 (Cray Valley Products) and 5 parts propylene glycol methyl ether acetate was screen printed through a 100T mesh silk screen on to bare FR4 epoxy glass laminate. The adhesive was dried to give a dry film weight of 5-8 microns.

A photocurable resin was prepared by dissolving an epoxy resin (40 parts) in trimethylol propane triacrylate (30 parts), then reacting with acrylic acid (12 parts), benzoic acid (4 parts) in the presence of trace proportions of a UV inhibitor and a catalyst. The resulting acrylated resin was then carboxylated using tetrahydrophthalic anhydride to give an acid value of 57mg KOH/gm. This was mixed in the following formulation (Coating A):

Coating A:

Material	Parts
Photocurable resin	35
TMPEOTA	5
Hydroxyethyl methacrylate	14
2-Ethyl Anthroquinone	3
Antifoam	0.5 (SAG100, OSI)
Talc	22
Silica	7
DEN438 (3)	10
Pigment Concentrate	3
Dicyandiamide (Thermal cure catalyst)	0.5
(3) Epoxy Resin, ex Dow Chemicals	

Coating A was screen printed through a 32T mesh silk screen and cured under a UV cure unit at an exposure level of 1,000mj/cm². The resulting cured film was 80 microns thick.

A photoimageable resin was produced by reacting an epoxy resin (40 parts) dissolved in propylene glycol diacetate (30.7 parts), with acrylic acid and benzoic acid (12 parts and 3 parts respectively) in the presence of trace proportions of a UV inhibitor and a catalyst. The resulting acrylated resin was then carboxylated with tetrahydrophthalic anhydride (14 parts). This photoreactive resin was then incorporated into the following photoimageable ink formula:

	21	
Material		Parts
Photoreactive Resin		62
Irgacure 907 (4)		5
Propylene Glycol Diacetate		3
Barium sulphate		21
Talc		5
Colour concentrate		4

(4) Photoinitiator, ex Ciba Geigy

This formulation was printed on to the photocured layer of Coating A using a 100T mesh silk screen and dried to give a tack free finish. The resultant film was 12 microns thick. The resist layer was then photoimaged through suitable art work and the desired pattern developed using 0.6% w/w sodium carbonate solution at 40°C.

A conductive formulation with the following constituents:

Material	Parts
Copper powder	40
Silver powder	30
Glycerol phthalate	14
Alpha™ 850 flux	8
Ethanol	8

was screen printed through a 32T mesh silk screen with a soft squeegee, ensuring that the grooves in the resist surface were filled with conductive material. The solvent was then driven from the ink by heating the board to 80°C for 15 minutes.

22

The completed board was then treated with a 10%w/w solution of sodium hydroxide to strip away the thin layer of photoimageable resist and any extraneous conductive ink from the board surface.

The completed board was then subjected to vapour phase reflow at 215°C to produce a coherent metal track system defined by the image in the resist layer, which could then be soldered. The circuit produced showed good conductance and resistance to stripping of the tracks by tape testing.

EXAMPLE 11

An adhesive was prepared by dissolving 50 parts Epikote 1001 (Shell Chemicals) in propylene glycol (50 parts). This adhesive was applied by airless spraying to a piece of plain FR2 paper-phenolic laminate and dried to yield an adhesive coating of 10-12 microns thickness.

A photocurable resin was prepared by mixing the following constituents:

Material	Parts
Alnovol PN320 (5)	31
Hydroxyethyl methacrylate	49
Talc	9
Silica	6
SAG 100 (6)	2
Phthalocyanine blue	1
Benzyl dimethyl ketal	1
Citric acid	1

(5) Phenolic resin, ex Hoechst Chemicals

(6) Silicon defoamer, ex OSI Specialities

This material was mixed with a thermal cure catalyst made up as follows:

Material	Parts
Epoxy resin	47
N-methyl pyrrolidone	35
Dipropylene glycol methyl ether	14
Epikure 143FF (7)	4

(7) Epikure 143FF, ex Shell Chemicals

in the ratio of 10 parts photocurable ink to one part catalyst. The mixed ink was silk screen printed through a 32T mesh silk screen and dried at 90°C for 15 minutes to give a dry film thickness of 50 microns. The dried board was then given a UV cure of 1500mj/cm².

A photoimageable resist (ImagecureTM) was applied to the surface of the photocurable resist layer by curtain coating. The ink was dried to a tack free finish by heating to 90°C for 15 minutes and then photoimaged through suitable art work. The image was developed using 0.6% w/w sodium carbonate to yield a board with the desired track design etched into its surface.

A conductive ink of the following formulation was then forced into the tracks by drawing a soft rubber squeegee loaded with the ink across the boards surface.

Material	Parts
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24

Copper powder	40
Tin/Lead powder	30
Glycerol phthalate	14
Alpha 850 flux	8
Acetone	8

The photoimageable layer was then stripped from the board surface by wiping with propylene glycol methyl ether acetate, taking any conductive ink overprinted on its surface with it.

The conductive ink was then reflowed and soldered by passing the board over a solder wave at 238°C to yield a conductive, coherent track pattern showing good reproducibility of the artwork used.

EXAMPLE 12

XV501TSM (Imagecure™) was silk screen printed through a 90T mesh onto a piece of glass epoxy laminate and dried at 90°C for 20 minutes to form an adhesive layer.

A conductive ink comprising

Copper powder	50
65/35 Sn-Pb	30
Glycerol Phthalate flux	10
Alpha™ 850	5
Isopropyl ether acetate	5

25

was manufactured by using a silverson H.S.S. then triple roll milled to give good wetting out of the metal and removal of air.

This ink was screen printed through a stainless steel mesh to give an electrical test pattern and dried for 30 minutes at 90°C. The resultant circuit had a resistivity of 500×10^{-5} ohms cm at this stage. The pattern was then reflowed at 215°C for 2-3 seconds, to give a continuous track with an electrical resistivity of less than 10^{-5} ohms cm.

EXAMPLE 13

As for Example 12 except that the conductive ink formulation was

Copper powder	28
65/35 Sn-Pb powder	28
Silver flake	28
Glycerol phthalate	7
2 Isopropyl ether acetate	19

This gave good conductivity matching Example 13 and was shelf life stable.

Reflow was carried out on a Sikama reflow bench with predry/reflow carried out in line with 3 minutes each at 80°C, 100°C, 200°C, 250°C.

This ink could only be soldered after electroless nickel gold plating.

EXAMPLE 14

As for Example 13 but

80/10/10/250 (8)	28
65/35 Sn-Pb powder	28
Ag flake	28

Glycerol Phthalate 7 26

2 Isopropyl ether acetate 19

(8) Tin lead coated copper powder, ex Eckart

The tin lead coating on the copper reduces the tendency to oxidation, improves both the reflow and conductivity, with an improvement in solderability over Example 13.

In the light of this disclosure, modifications of the described embodiment and examples, as well as other embodiments and examples, all within the scope of the present invention as defined by the appended claims, will now become apparent to persons skilled in the art.

CLAIMS

1. A method of forming a conductive path of an electrical circuit board, the method comprising applying an adhesive to a circuit board substrate and applying a conductive ink over the adhesive in a pattern corresponding to the conductive path.
2. A method of forming a conductive path of an electrical circuit board, the method comprising applying a photoimageable layer to a circuit board substrate, subjecting the photoimageable layer to a photoimaging and developing process to form a track in the photoimageable layer, the track corresponding to the said conductive path, and introducing a conductive ink into the track to form a conductive ink pattern.
3. A method according to claim 2, wherein the track is formed with an undercut region in side walls thereof.
4. A method according to any preceding claim, further comprising a step of heating the conductive ink pattern to effect reflow or sintering of a metallic component of the ink.
5. A method according to claim 4 when dependent upon claim 1, comprising the further step of applying a photoimageable layer over the adhesive, subjecting the photoimageable layer to a photoimaging and developing process to form a track in the photoimageable layer, the track corresponding to the said conductive path, the conductive ink being introduced into the track prior to the heating step.

6. A method according to claim 5, wherein the heating step is carried out such as to effect simultaneous curing of the adhesive, bonding of the conductive ink to the adhesive layer and reflow or sintering of the metallic component of the ink.
7. A method according to any preceding claim, wherein the conductive ink is applied in the said pattern by means of a stencil which is removed before the heating step.
8. A method according to any preceding claim, wherein the conductive ink is applied in the said pattern by means of a squeegee or similar scraping action.
9. A method according to any of claims 2, 3, 5 or 6, wherein the conductive ink is introduced into the track by curtain coating.
10. A method according to any of claims 2, 3, 5 or 6, wherein the conductive ink is introduced into the track by spray application.
11. A method according to any of claims 2, 3, 5 or 6, wherein the conductive ink is introduced into the track by inkjet application.
12. A method according to any of claims 2, 3, 5 or 6, wherein the conductive ink is introduced into the track by pressure injection .
13. A method according to any of claims 2, 3, 5, 6 or 9 - 12, wherein the developing process is effected by applying on alkali solution or an organic solvent to the photoimaged layer.

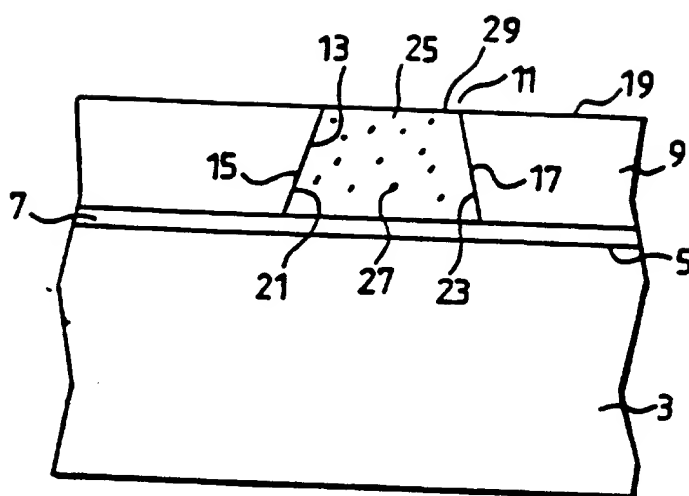
14. A method according to any of claims 2, 3, 5 6 or 9 - 13, wherein the photoimageable layer contains a photoinitiator.
15. A method according to claim 14, wherein the photoinitiator is of a type which preferentially hardens the surface of the photoimageable layer.
16. A method according to any of claims 2, 3, 5, 6 or 9 - 15, wherein the photoimageable layer contains a pigment or other solid material for limiting penetration of radiation into the body of the photoimageable layer.
17. A method according to any of claims 2, 3, 5 6 or 9 - 16, wherein the photoimageable layer is applied in two or more separate applications.
18. A method according to claim 17, further comprising a step of removing an upper layer of the photoimageable layer and any excess metal.
19. A method according to any of claims 4, 5, 6 or 9 - 18, wherein the heating step is effected by progressively raising the temperature of the conductive ink such that the ink dries at a first temperature and then the metallic component sinters or melts at a second temperature, higher than the first temperature.
20. A method according to any of claims 4, 5, 6 or 9 - 19, wherein the metallic component is supported in a flux component of the conductive ink and comprises a mixture of metals or alloys having a relatively low melting point component and a relatively high melting point component.

30

21. A method according to claim 20, wherein the relatively low melting point component has a melting point in the range of from 100°C to 250°C.
22. A method according to claim 20 or claim 21, wherein the relatively high melting point component has a melting point in the range of from 300°C to 1455°C.
23. A method according to any of claims 20 to 22, wherein the relatively low melting component comprises at least one metal selected from tin, lead, silver, bismuth, antimony and indium or an alloy of at least any two or more of such metals.
24. A method according to any of claims 20 to 23, wherein the relatively high melting component comprises at least one metal selected from tin, silver, copper, zinc, iron, manganese nickel and cobalt or an alloy of at least any two or more of such metals.
25. A method according to any of claims 20 to 24 when dependent upon claim 19, wherein the said second temperature is higher than the melting point of the relatively lower melting point component and the resulting conductive path has a higher melting point than that of the relatively lower melting point component.
26. A method according to any of claims 20 to 25, wherein the flux component comprises a wetting agent and a reactive agent capable of reacting with copper, the wetting agent being incorporated in the flux in advance and the reactive agent being incorporated immediately prior to application.
27. A method according to any of claims 1, 5 and 6, wherein the adhesive is a single component adhesive.

28. A method according to any of claims 1, 5 and 6, wherein the adhesive is a two-component adhesive.
29. A method according to any of claims 1, 5, 6, 27 and 28, wherein the adhesive comprises at least one resin selected from epoxy resins, novolak resins, epoxy novolak resins, acrylate resins and polyamide resins, together with a catalyst for effecting curing of said resin at an elevated temperature.
30. An electrically conductive composition comprising a metallic component and a flux, the composition being substantially free of any resin or reactive monomer or polymer.
31. A composition according to claim 30, the composition being completely free of any resin or reactive monomer or polymer.
32. An electrically conductive composition according to claim 29 or claim 30, wherein the metallic component comprises a mixture of metals or alloys, having a relatively low melting point component and a relatively high melting point component.
33. A composition according to claim 32, wherein the relatively low melting component comprises at least one metal selected from tin, lead, silver, bismuth, antimony and indium or an alloy of at least any two or more of such metals.
34. A composition according to claim 32 or claim 33, wherein the relatively high melting component comprises at least one metal selected from tin, silver, copper, zinc, iron, manganese nickel and cobalt or an alloy of at least any two or more of such metals.

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FIG.1

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/GB 96/00105

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H05K3/10 H05K3/38 H05K1/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,24 11 988 (E. I. DU PONT DE NEMOURS AND COMPANY) 19 September 1974 see the whole document	1,4,7,8, 19-25, 27,29-34
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A	DE,A,22 31 614 (WEGNER) 10 January 1974 see the whole document	8
Y	---	2,5,6
X	DE,B,11 28 493 (SIEMENS-ELECTROGERÄTE AG) 26 April 1962 see the whole document	1,30
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A	---	4,29
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

2 April 1996

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INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/GB 96/00105

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p style="text-align: center;">---</p> PATENT ABSTRACTS OF JAPAN vol. 14 no. 541 (E-1007) ,29 November 1990 & JP,A,02 231788 (SHARP CORP.) 13 September 1990, see abstract	2,8
A	<p style="text-align: center;">---</p> US,A,3 800 020 (PARFET) 26 March 1974 see column 3, line 1 - line 25	20-24
X		30-34
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X		30-34
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A	<p style="text-align: center;">---</p> EP,A,0 613 330 (SIEMENS AG) 31 August 1994 see column 2, line 40 - line 56 <p style="text-align: center;">-----</p>	4,10,11, 20-24, 30-34

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Intern. Application No
PCT/GB 96/00105

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